Patent Claims

1. Non-pressurized method for the continuous production of alkyl esters of higher fatty acids, especially biodiesel, from fatty acid triglyceride starting mixtures containing free fatty acids, with an integrated combination of acid esterification and basic transesterification, including

   a) single or multiple esterification of the free fatty acids in separate esterification devices connected with each other, with a C_1- to C_4- mono alcohol in the presence of an acid catalyst and glycerine as a dragging agent, at 60°C to 65°C while an esterification mixture is produced,

   b) partial purification of the esterification mixture via partial separation of the dragging agent, acid catalyst and unconverted C_1- to C_4- mono alcohol,

   c) transesterification of the fatty acid triglycerides, carried out at least twice, in separate transesterification devices connected with each other, with a C_1- to C_4- mono alcohol in the presence of a base catalyst at 60°C to 65°C while a transesterification mixture is produced, and

   d) purification of the transesterification mixture via separation of the basic catalyst, unconverted C_1- to C_4- monoalcohol and the glycerine produced

during transesterification, by means of treatment using water in at least one separator with subsequent drying,

characterised by the fact that the C_1- to C_4- mono alcohol used for esterification, the conveying agent glycerin used for esterification and the water used for purification of the transesterification mixture are at least partially recovered from the esterification and transesterification mixtures and that after purification the acid and base catalysts from the esterification and transesterification mixtures are converted, resulting in the production of a salt suitable for use as a fertilizer.

2. Method according to claim 1, whereby the fatty acid triglyceride initial mixtures containing free fatty acids are used or unused, unpurified or purified vegetable, animal or industrial oils or fats or mixtures thereof with a free fatty acid content of 0 % to 100 %.

3. Method according to claim 1 or 2, whereby the unpurified oils or fats are selected from the group comprising soapstock, brown grease, yellow grease, industrial tallow, industrial lard, oil used for deep-frying, animal fat waste products, edible tallow, unpurified crude vegetable oils, unpurified animal fats or mixtures thereof.

4. Method according to claim 3, whereby the unpurified crude vegetable oils are

selected from the group comprising rapeseed oil, soybean oil, sunflowerseed oil, palm oil, maize germ oil, cotton seed oil, palm kernel oil and coconut oil.

5. Method according to one of the claims 2 to 4, whereby the unpurified starting mixtures are purified prior to esterification.

6. Method according to claim 2, whereby the purified oils or fats are refined or semi-refined products of vegetable or animal oils or fats.

7. Method according to claim 6, whereby the vegetable or animal oils or fats are selected from the group comprising rapeseed oil, soybean oil, sunflowerseed oil, palm oil, maize germ oil, cotton seed oil, palm kernel oil or coconut oil.

8. Method according to one of the preceding claims, whereby the esterification device is a column with or without ceramic or metallic packings or packings made of wire fabric.

9. Method according to one of the preceding claims, whereby the C_1- to C_4- mono alcohol used for esterification is methanol or ethanol.

10. Method according to one of the preceding claims, whereby the acid catalyst used for esterification is sulphuric acid or p-toluol sulfonic acid.

11. Method according to one of the preceding claims, whereby the free fatty acids are esterified 2 to 8 times in separate columns consecutive to and connected with each other, depending on the fatty acid content of the starting mixtures.

12. Method according to claim 11, whereby the obtained esterification mixture from one column is conducted from that column into the consecutive column and whereby after the addition of a mixture containing a dragging agent, a mono alcohol and acid catalyst, the esterification mixture is esterified again.

13. Method according to claim 12, whereby different amounts of acid catalyst are introduced into the separate columns.

14. Method according to claim 12 or 13, whereby a part of the esterification mixture from one column is conducted to the consecutive column and whereby a part of the esterification mixture is re-conducted into the preceding column.

15. Method according to one of the claims 11 to 14, whereby the esterification mixture is partially purified prior to being conveyed into the consecutive column.

16. Method according to claim 15, whereby a mixture containing dragging agent, acid catalyst, unconverted mono alcohol and water produced during esterification is separated as the heavy phase via phase separation from the esterification mixtures

and is conveyed to devices for the purification and separation of the components of the mixture.

17. Method according to claim 16, whereby the heavy phase is conducted into a drying device for the separation of mono alcohol and water.

18. Method according to claim 17, whereby water is separated via molecular sieves or micro filters within the drying device or whereby a mono alcohol and water mixture is evaporated via distillation.

19. Method according to claims 17 or 18, whereby the mono alcohol and/or the mono alcohol – water mixture is conducted from the drying device into a rectification device for further purification.

20. Method according to claim 19, whereby the mono alcohol purified in the rectification device, with a water content of approximately 1 % to 2 % suitable for use in columns due to a higher fatty acid content, is re-conducted from the rectification device into the esterification device.

21. Method according to claim 17 or 18, whereby a partial flow of the mixture obtained in the drying device after separation of mono alcohol and water and containing dragging agent and acid catalyst, is re-conducted from the drying

device into the esterification device, and whereby a partial flow of the above-mentioned mixture is conducted into an acidification device.

22. Method according to one of the preceding claims, whereby the esterification mixture obtained after esterification in the last esterification column is conducted into an extraction column and is subjected to extraction method in that column while pure mono alcohol or a mono alcohol –dragging agent mixture for the removal of non-esterified free fatty acid is being utilized.

23. Method according to one of the preceding claims, whereby an esterification mixture is obtained on completion of the last esterification method in the last esterification column or on completion of the extraction method in the extraction column and whereby almost all free fatty acids have been esterified and whereby the above-mentioned mixture has an acid number of approximately 1 to 0.5 and a maximum water content of 0.5 %.

24. Method according to claim 23, whereby the esterification mixture is conducted into a transesterification device connected to the last esterification column or to the extraction column for the basic transesterification of the fatty acid glycerides.

25. Method according to claim 24, whereby prior to transesterification one or several fatty acid triglyceride starting mixtures with a free fatty acid content of 0 % to 1 % are added to the esterification mixture.

26. Method according to claim 25, whereby the starting mixture added to the esterification mixture is a refined or semi-refined product of rapeseed oil, soybean oil, sunflowerseed oil, palm oil, maize germ oil, cotton seed oil, palm kernel oil and coconut oil or a mixture thereof.

27. Method according to one of the claims 24 to 26, whereby the esterification mixture to be transesterified and the starting mixture that was added if required are transesterified 2 to 6 times depending on the composition of the total mixture in separate transesterification devices that are arranged consecutively to each other and are connected with each other.

28. Method according to claim 27, whereby the transesterification devices are columns with or without ceramic or metallic packings or packings made of wire fabric.

29. Method according to one of the claims 24 to 28, whereby the C_1- to C4- mono alcohol used for transesterification is methanol or ethanol.

30. Method according to one of the claims 24 to 29, whereby the base catalyst used for transesterification is potassium hydroxide, sodium hydroxide or sodium methylate.

31. Method according to one of the claims 24 to 30, whereby the transesterification mixture obtained in a column is subjected to preliminary purification.

32. Method according to claim 31, whereby a mixture of mono alcohol, base catalyst and glycerine is separated as the heavy phase via phase separation from the transesterification mixture and is conducted for further purification and separation of the components to an acidification device and subsequently to a separator arranged consecutively to the acidification device.

33. Method according to claim 21 or 32, whereby the heavy phase separated from the transesterification mixture is mixed in the acidification device with the partial flow of the dragging agent and acid catalyst mixture that was separated following esterification and conducted into the acidification device, whereby the partial flow is proportioned in such a way that the base catalyst of the heavy phase is neutralised and the heavy phase is sufficiently acidified.

34. Method according to one of the claims 31 to 33, whereby the pre-purified transesterification mixture is conducted into a separator for further purification.

35. Method according to claim 34, whereby a water-containing mixture comprising mono alcohol, soap, base catalyst and glycerine is separated in the separator from the transesterification mixture with water.

36. Method according to claim 35, whereby pH-conditioned water or buffered water, especially condensation water or de-ionized water, are used.

37. Method according to one of the claims 34 to 36, whereby the purified transesterification mixture is conducted from the separator to a consecutive transesterification column for further transesterification.

38. Method according to one of the claims 34 to 36, whereby the purified transesterification mixture of the last transesterification column is conducted out of the separator into at least one additional separator for further purification.

39. Method according to claim 38, whereby the transesterification mixture from the at least one additional separator is conducted into a drying device where it is dried and purified.

40. Method according to claim 39, whereby following purification in the drying device a product mixture corresponding to biodiesel and comprising mainly C_1- to C_4- alkyl esters of the free fatty acids and C_1- to C_4- alkyl esters of the higher fatty acids is obtained from the fatty acid triglycerides.

41. Method according to one of the claims 34 to 36 or 38, whereby the water-containing mixture of mono alcohol, soap, base catalyst and glycerine separated

from the transesterification mixture in the separator is conducted into the acidification device and then into a consecutive separator.

42. Method according to claim 32 or 41, whereby the fatty acids formed during transesterification are partially separated from the remaining components of the water-containing mixture in the separator that is consecutive to the acidification device and are re-conducted into the esterification device.

43. Method according to claim 42, whereby the remaining components of the water-containing mixture are conducted from the separator into the rectification device.

44. Method according to claim 43, whereby the mono alcohol is separated in the rectification device from the remaining components of the water-containing mixture and is re-conducted to the esterification device in a purified state, whereby the water content of the purified mono alcohol is approximately 1 % to 2 %, preferably 0.1 %.

45. Method according to claim 44, whereby the remaining components of the water-containing mixture are conducted from the rectification device into an evaporation device.

46. Method according to claim 45, whereby the water is separated in the evaporation device and is re-conducted into the separators.

47. Method according to claim 46, whereby the mixture comprising glycerine, acid catalyst and base catalyst is conducted into a distillation device for further purification.

48. Method according to claim 47, whereby the glycerine is separated in the distillation
device from the catalysts and is partially re-conducted into the esterification device in a purified state after filtration via a filtration device.

49. Method according to claim 47, whereby acid and base catalyst are conducted from the distillation device into a thin-layer-evaporation device where the acid and base catalysts are converted, resulting in the formation of a salt suitable as fertilizer.

50. Device for the production of biodiesel from fatty acid triglyceride initial mixtures containing free fatty acids, including in an integrated combination an esterification unit (3) with at least two esterification devices (9, 171, 173, 175, 177, 11) for the esterification of the free fatty acids, a transesterification unit (5) consecutive to and connected with the esterification device with at least two transesterification devices (15, 17) for the transesterification of the fatty acid triglycerides, a purification unit (6) consecutive to and connected with the transesterification device (5) for purifying the produced biodiesel and a

purification unit (8) consecutive to and connected with the transesterification device (5) for the purification and separation of the agents used in the esterification unit (3) and/or transesterification unit (5) and/or purification unit (6), characterised by the fact that the purification unit (8) is connected by means of at least one feeding (101) and at least one discharge (127, 153, 155) with the esterification unit (3), so that the agents used in the esterification unit (3) and the transesterification unit (5) are simultaneously purified and separated in the purification device (8) and that the agents used for esterification are recycled into the esterification unit (3).

51. Device according to claim 50, whereby the agents used in the esterification unit (3) are a C_1- to C_4- mono alcohol, an acid catalyst and a dragging agent, whereby the agents used in the transesterification device (5) are a base catalyst and the C_1- to C_4- mono alcohol and whereby water is the agent used in the purification unit (6).

52. Device according to claim 50 or 51, whereby the esterification unit (3) is provided with 2 to 8 consecutive esterification devices (9, 171, 173, 175, 179, 11) that are connected to each other.

53. Device according to one of the claims 50 to 52, whereby the esterification devices (9, 171, 173, 175, 179, 11) are designed as columns.

54. Device according to claim 53, whereby the last column (11) is designed as an extraction column.

55. Device according to one of the claims 50 to 54, whereby the esterification devices (9, 171, 173, 175, 179, 11) are connected via one inlet conduit (41, 185, 187, 189, 191, 201) each for conveying the products formed in one device as the light phase into the consecutive device.

56. Device according to claim 55, whereby the feeding pipes (41, 185, 187, 189, 191, 201) are provided with a subsidiary pipe (39) for re-conducting a partial flow of the products formed in the esterification devices (9, 171, 173, 175, 179, 11) into the same or into a preceding esterification device.

57. Device according to one of the claims 50 to 56, whereby at least one esterification device (9, 171, 173, 175, 179, 11) is connected to a mixing device (35, 199) via afeeding (37, 169) for conducting a mixture of C_1- to C_4- mono alcohol, acid catalyst and dragging agent produced in the mixing device (35, 199) into the esterification device (9, 171, 173, 175, 179, 11).

58. Device according to claim 57, whereby two or more or each of the esterification devices (9, 171, 173, 175, 179, 11) are each connected to one separate mixing device (35, 199) via separate feedings (37, 169) for conducting mixtures with

identical or different concentrations of C_1- to C_4- mono alcohol, acid catalyst and dragging agent into the esterification devices (9, 171, 173, 175, 179, 11).

59. Device according to one of the claims 50 to 58, whereby the esterification devices (171, 173, 175, 179, 11) are connected via one feeding (181, 183, 193, 195) each for conveying at least a partial flow of the heavy phase, obtained via phase separation after esterification in an esterification device and containing unconverted glycerine, unconverted mono alcohol and unconverted acid catalyst, into the preceding esterification device (9, 171, 173, 175, 179).

60. Device according to claim 59, whereby the feeding (181, 183, 193, 195) passes through a drying device (197) in order to remove water and/or mono alcohol from the heavy phase.

61. Device according to claim 60, whereby the drying device (197) is designed as a distillation device for the evaporation of a water - mono alcohol mixture, or as a molecular sieve or micro filter in order to remove water as a permeate.

62. Device according to one of the claims 59 to 61, whereby the feeding (181, 183, 193, 195) is provided with a subsidiary pipe (203, 205) for conveying a partial flow of the heavy phase into the same esterification device (171, 173, 175, 179, 11).

63. Device according to one of the claims 50 to 62, whereby the esterification devices (9, 171, 173, 175, 179, 11) are connected with the transesterification unit (5) via at least one feeding (47) for conveying the products formed in the esterification devices (9, 11) into the transesterification device (5).

64. Device according to one of the claims 50 to 63, whereby the transesterification unit (5) is equipped with 2 to 4 transesterification devices (15, 17) arranged consecutively and connected with each other.

65. Devices according to claim 64, whereby the transesterification devices (15, 17) are designed as columns.

66. Device according to claim 64 or 65, whereby the transesterification devices (15, 17) are connected with the purification unit (6) via at least one feeding (105, 106) for conveying the products formed in the transesterification devices (15, 17) into the purification unit (6).

67. Device according to one of the claims 50 to 66, whereby the purification unit (6) is equipped with at least 4 separators (71, 73, 75, 77), arranged consecutively to and connected with each other, and a drying device (159) for the purification of the obtained product.

68. Device according to claim 67, whereby the separators (71, 73, 75, 77) are connected with the drying device (159) via afeeding (57) for conducting the products that were separated from the base catalyst, mono alcohol, acid catalyst and dragging agent in the separators (71, 73, 75, 77) into the drying device (159).

69. Device according to claim 67 or 68, whereby the drying device (159) is equipped with an outlet conduit (163) for the end products purified in the drying device (159).

70. Device according to claim 67 or 68, whereby the separators (71, 73, 75, 77) are connected with the purification unit (8) via the feedings (107, 109) for conducting the mixture of base catalyst, mono alcohol, acid catalyst and dragging agent separated in the separators (71, 73 75, 77) into the purification unit (8).

71. Device according to one of the claims 50 to 70, whereby the purification unit (8) is equipped with at least one drying device (97), an acidification device (103), a separator (113), a rectification device (117), an evaporation device (121), a distillation device (131), a thin-layer-evaporation device (139) and a filtration device (147).

72. Device according to one of the claims 50 to 71, whereby the esterification devices (9, 11) are connected with the drying device (97) via at least one feeding (95) for conducting a mixture comprising unconverted C_1- to C_4- mono alcohol, acid

catalyst and dragging agent, obtained in the esterification devices via phase separation, into the drying device (97).

73. Device according to claim 72, whereby the drying device (97) is connected with the rectification device (117) via afeeding (125) for conveying the C_1- to C_4- mono alcohol separated in the drying device into the rectification device (117).

74. Device according to claim 72 or 73, whereby the drying device (97) is connected with the acidification device (103) via a feeding (101) for conducting the mixture of acid catalyst, conveying agent and traces of C_1- to C_4- mono alcohol, separated in the drying device (97), into the acidification device (103).

75. Device according to claim 71 or 74, whereby the acidification device (103) is connected with the separators (71, 73, 75, 77) via the feedings (107, 109).

76. Device according to claim 74 or 75, whereby the acidification device (103) is connected with the separator (113) via a feeding (111) for conveying the mixture that was acidified in the acidification device (103) into the separator (113).

77. Device according to claim 76, whereby the separator (113) is connected with the esterification unit (3) via a feeding (155) for re-conducting the fatty acid separated in the separator (113) into the esterification unit (3).

78. Device according to claim 76 or 77, whereby the separator (113) is connected with the rectification device (117) via a feeding (115) for conveying the water-containing mixture of acid catalyst, base catalyst and traces of the mono alcohol formed in the separator (113) into the rectification device (117).

79. Device according to claim 78, whereby the rectification device (117) is connected with the esterification unit (3) via a feeding (127) for re-conducting the mono alcohol purified in the rectification device (117) into the esterification unit (3).

80. Device according to claim 78 or 79, whereby the rectification device (117) is connected via a feeding (119) with the evaporation device (121).

81. Device according to claim 80, whereby the evaporation device (121) is equipped with a feeding (123) serving to convey the water purified in the evaporation device (121).

82. Device according to claim 80 or 81, whereby the evaporation device (121) is connected with the drying device (131) and the distillation device (135) via feedings (129, 133) for conveying the mixture of glycerin, acid catalyst and base catalyst, separated in the evaporation device (121), into the device (135).

83. Device according to claim 82, whereby the distillation device (135) is connected with the thion-layer-evaporation device (139) via afeeding (137) for conveying the acid and base catalysts separated in the device (135) into the evaporation device (139).

84. Device according to claim 83, whereby the thin-layer-evaporation device (139) is equipped with a pipe (141) serving as adischarge for the conversion product of the base and acid catalyst that is suitable for use as a fertilizer.

85. Device according to claim 83, whereby the distillation device (135) is connected with the filtration device (147) via a feeding (145) for conveying the glycerin into the filtration device (147).

86. Device according to claim 85, whereby the filtration device (147) is connected with the esterification unit (3) via a feeding (149) in order to re-cycle a partial flow of the glycerine purified in the filtration device so that it can be reused as dragging agent.